

A  
Project Report  
on  
**“ EXPERIMENTAL STUDY ON SYNTHESIS, CHARACTERIZATION  
AND APPLICATIONS OF NOVEL ADSORBENTS “**

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In partial fulfillment for the award of the degree of  
**Bachelor of Technology**  
in  
**Chemical Engineering**



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*Certificate*

*Certified that this Project thesis entitled*  
***“ Experimental study on synthesis, characterization and applications of novel adsorbents ”***  
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*during the year 2013-2014 in partial fulfillment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela has been carried out under my supervision and this work has not been submitted elsewhere for a degree.*

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## ABSTRACT

Novel materials usher new technologies and since time immemorial mankind have been thriving to discover and develop new materials to benefit them. In this project work, two relatively new porous materials *viz.* MCM-41 and Cu-BTC were synthesized, following standard recipes. Detailed characterizations were carried out to ascertain the products formed, following techniques like Scanning Electron Microscopy (SEM), Powder X-ray diffraction (PXRD) analysis, BET surface area analysis and Laser particle Size Analysis. SEM images revealed contrasting surface morphology for the synthesized products. MCM-41 showed discontinuity in crystal formation with imperfections and distribution in porous networks whereas Cu-BTC showed a much uniform growth of crystals with regular sizes, shapes and porous network. Powder X-ray diffraction also corroborated the findings and it showed that as-synthesized MCM-41 was amorphous in nature whereas Cu-BTC was crystalline. The BET surface area measurements data showed that the specific surface area of MCM-41 was *ca.* 1200 m<sup>2</sup>/gm and for Cu-BTC, the value stood at *ca.* 1500 m<sup>2</sup>/gm. Laser particle size analysis for MCM-41 also showed a wider distribution of particles, using water as the dispersant medium. A new variant of MCM-41 was also synthesized by replacing the costly Si source (Tetraethyl orthosilicate) with cheaper source (Sodium silicate solution). Surface area data showed a much lesser surface area of *ca.* 36 m<sup>2</sup>/gm. This variation could be attributed to post synthesis treatments and presence of cetyl tertiary butyl ether (CTAB) in the framework as a template. Owing to higher surface area Cu-BTC was used for studying the degradation of polystyrene. The study showed affirmative results in the degradation temperature of polystyrene.

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## ABBREVIATIONS

AIP	-	Aluminum isopropoxide
BET	-	Brunauer, Emmett and Teller
DMF	-	Dimethyl Formamide
H <sub>2</sub> BDC	-	Benzene dicarboxylic acid
H <sub>3</sub> BTC	-	Benzene tricarboxylic acid
HDPE	-	High Density Polyethylene
HKUST	-	Hong Kong University of Science and Technology
LDPE	-	Low Density Polyethylene
MCM	-	Mobil Composition of Matter
MOF	-	Metal Organic Framework
PXRD	-	Powder X-Ray Diffraction
SEM	-	Scanning Electron Microscope
STP	-	Standard Temperature Pressure
TEOS	-	Tetraethoxysilane
TGA	-	Thermo gravimetric Analysis

## LIST OF SYMBOLS

$x$	:	relative pressure $P/P_0$
$V$	:	the STP volume of the adsorbate
$V$	:	the STP volume of the amount of adsorbate required to form monolayer
$c$	:	the equilibrium constant
$\theta$	:	incident angle
$d$	:	spacing between the planes
$n$	:	any integer
$\lambda$	:	the wavelength of the incident beam.

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## 1. INTRODUCTION

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### 1.1. PRELUDE

The separation of vapors and gasses is an important process in various chemical industries, from the separation of nitrogen from air to that of hydrocarbons. The idea of separation procedures is likewise recognized to be part and parcel of Chemical Engineering which predominantly refers to the partition of a mixture into two separate components instead of two components changing in their composition. Despite the fact that cryogenic refining systems are still an imperative separation system and utilized industrially, the adsorptive gas partitions utilizing diverse metal organic frameworks and zeolites are currently getting to be progressively extremely famous.

Various unit operations are used to separate mixtures based on the purity of required product, mixtures' chemical properties, kind of mixture and scale of production, including different techniques like adsorption, refining, stripping, absorption, extraction and membranes. At the same time among all the specified advances, adsorption science has developed as of late as an alluring choice for intrinsic focal points it has, for example, adsorbents with efficient surface area, capacity to tune up as per the procedure variables and accessibility of an extensive variety of materials. Vast number of examination has been done in this field and related region has additionally helped the advancement of porous solids especially the adsorbents like zeolites and MOFs because of its use in adsorption, catalysis and purification and separation applications.

### 1.2. BACKGROUND OF PRESENT WORK

Novel materials usher new technologies and since time immemorial mankind have been thriving to discover and develop new materials to benefit them. Metal Organic

Frameworks (MOFs) represent a new family of novel adsorbents and Zeolites are more conventional and have been in vogue since 1950s. They have high surface area ( $\sim 300$  to  $5000 \text{ m}^2/\text{g}$ ) and large pore volume ( $0.3$ - $1.5 \text{ cc/g}$ ) and low to moderate heat of adsorption ( $\sim 12$  to  $30 \text{ kJ/mol}$  at moderate coverage). All these features make these classes of adsorbents very attractive from an application point of view. However, certain challenges remain before these materials can be exploited. It has often been found that the materials synthesized in different laboratories (or even in different batches from the same lab) have different characteristics and it is often difficult to reproduce experimental results with accuracy. This variation is usually attributed to the difference in degree of purity of the materials as well as residual solvent used during synthesis which is left inside the pores. Moreover, some of these materials are known to have low thermal stability and decompose on exposure to moisture for long periods of time.

### **1.3. MAIN OBJECTIVES**

In this project work, emphasis has been stressed upon to synthesize and characterize two different porous frameworks *viz.* MCM-41 and Cu-BTC. It is however important to highlight the fact that MCM-41 is a type of zeolites and Cu-BTC is one of the most established Metal Organic framework (MOF).

It is also aimed to synthesize a new variant/derivative of MCM-41 by replacing the costly source of Si (TEOS) in the reaction stoichiometry with a regular source (Sodium silicate) and characterize it.

Based upon superior porous network and specific surface area it is aimed to screen out the best adsorbent material and carrying out heterogeneous polymer degradation study with polystyrene and figure out the degradation profile.

#### **1.4. THESIS SUMMARY**

There are five chapters in this thesis; Introduction, Literature Review, Experimental Works, Results and Discussions, Conclusions and Future Recommendations. All these chapters provide adequate details about both past and the present researches in this field, experimental methods followed and various research findings and their best possible explanations.

**Chapter 1** gives introduction of research in brief and comprehensive description of research background along with the objectives of this work and overview of the entire thesis.

**Chapter 2** enlightens us with the detailed literature reports relating to this field of adsorbents, their application and sequential events in their development.

**Chapter 3** describes the methods and procedures followed in synthesizing Al-MCM-41 and MOFs. Different quantitative estimation techniques for better quality are also explained in detail.

**Chapter 4** reports and interprets various results obtained during this study and experimentation. All the possible explanations for various observations are also given in detail.

**Chapter 5** concludes all the results and observations obtained during this study. Future recommendations are also suggested. The major highlights of this present work are also summarized.

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## 2. LITERATURE REVIEW

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This chapter is dedicated fully to discuss in detail the various reported works by different research groups in the various field of novel adsorbents, particularly focusing on the different aspects of development of Al-MCM-41 and MOFs. A comprehensive review on Al-MCM-41 and MOF is described in detail. The underlying principles of these adsorbents synthesis and their characterization are highlighted. Furthermore, various important prospective applications that are reported in the literature are also summarized.

### 2.1. GENERAL THEORY AND CLASSIFICATION OF POROUS SOLIDS

#### 2.1.1. FUNDAMENTALS OF ADSORPTION

A numerous processes (chemical, physical and biological) occur at the boundary between two phases, while numerous others are started at the interface[5]. Change in the concentration of given substance at interface as contrasted with the neighboring stages is alluded to as adsorption. Depending upon the different phases in contact, we can arrange this procedure into these fundamental frameworks: solid-gas, solid-fluid, fluid-fluid and fluid-gas [34]. Adsorption, on a cutting edge scale, bargains in a general sense with the solid-liquid and solid-gas interfaces. The "liquid" is typically referred to as a gas or liquid in contact with the surface of solids. The real adsorption framework is the principal thought in an adsorption happening at every interface. The true adsorption framework [5], on account of solid-gas retention, could be portrayed as an balance one being the adsorbent in contact with the bulk phase and the indicated interfacial layer. This layer includes 2 locales: the surface layer of the solid and the part of gas in the energy field of the solid surface. The "adsorption" deals with the methodology in which the molecules get gathered in the interfacial layer, however desorption is the inverse strategy of adsorption. Adsorption hysteresis [5] happens when the adsorption and desorption curves stray from each one in turn. Here the isotherm has a

hysteresis loop whose shape varies from one adsorption framework to other. Hysteresis [31] are fundamentally found with mesoporous solids, where the capillary condensation prevails. The material in the adsorbed state is known as the 'adsorbate', and that in the bulk gas/vapor stage before being adsorbed is alluded as the 'adsorptive'. The permeability of the adsorbate molecules into the bulk solid phase is termed as 'adsorption'. It is characterized as the equilibrium relation between the amount/ measure of the adsorbed material and the pressure /concentration in the bulk liquid phase with temperature being steady.

### **2.1.2. CLASSIFICATION OF POROUS SOLID MATERIALS**

The primary classification of adsorbents is based on two distinct types of surfaces:

- a) hydrophilic
- b) hydrophobic.

This behavior can be attributed to surface polarity (due to presence of ions in the structure) of different adsorbents. Polar adsorbents like activated alumina, silica gel, zeolites etc. show a great affinity towards the polar molecules but non-polar activated carbon shows little or no affinity towards polar adsorbates. The hydrophilic nature of zeolites is the polarity of heterogeneous surface whereas presence of the hydroxyl groups on surface of the activated alumina or silica gel is largely responsible for their 'hydrophilicity' due to hydrogen bond formation [34].

One of the most salient feature of any adsorbent is porosity [1]. A highly porous material possess a high total pore volume and specific surface area. Thus pore size distribution is a necessary consideration during physical characterization of different porous materials. Parameters like bulk crush strength, density and erosion resistance also have their importance while characterizing any solid adsorbent.

International Union of Pure and Applied Chemistry (IUPAC) [50] has categorized porous materials into 3 different categories based on pore size:

- a) microporous (<2 nm)
- b) mesoporous (2-50 nm)
- c) macroporous (>50 nm).

There exists an important difference between the various adsorbents, within the microporous regime. For adsorbents like activated carbon, silica gel and activated alumina there is wide distribution of micropore size, whereas in zeolites as adsorbent, since the crystal structure controls the micropore size, there is no distribution of pore size. This unique feature of zeolites gives diversifying results in adsorption properties and differ them from other conventional adsorbents.

## **2.2. GENERAL BACKGROUND ON VARIOUS POROUS MATERIALS**

In the last decades, the inclination towards porous solid material synthesis, their properties along with prospective applications have grown particularly due to huge efforts by research community in search of various high performance solids. The adaptability of porous substances for various applications [6] like separation, adsorption and purification, as well as catalysis have always been in favor of development of advanced materials which are capable of exhibiting properties that world has never ever seen. Nowadays interest towards the catalytic pyrolysis of waste plastics is growing rapidly. It produces selective and desired range of products along with reducing the reaction temperature.

The historical development relating to the development of various porous coordination polymers and MOFs [14] are relatively fresh and exemplifies number of interdisciplinary research fields which involve Chemical Engineering, Material Science, Chemistry and Nanotechnology. Even though the coordination chemistry of association of different metal atoms and organic was first reviewed in 1964 [9], reported by Robson and Hoskins in 1990 and 1989 respectively, found a way out for future research on MOF.



**Table 2.1** : Classification of zeolites based on pore size [55]

<b>Pore size (Å)</b>	<b>definition</b>	<b>Typical material</b>	<b>Ring size</b>	<b>Pore Diameter (Å)</b>	<b>reference</b>
>500	Macroporous				
20-500	Mesoporous	MCM-41		15-100	Beck et al, 1992a
<20	Microporous				
	Ultralarge pore	Cloverite	20	6.0-13.2	Estermann et al, 1991
		JDF-20	20	6.2-14.5	Jones et al, 1993
		VPI-5	18	12.1	Davis et al, 1988
		AlPO <sub>4</sub> -8	14	7.9-8.7	Dessau et al, 1990
	Large pore	Faujasite	12	7.4	Olson, 1970
		AlPO <sub>4</sub> -5	12	7.3	Bialek et al, 1991
		ZSM-12	12	5.5-5.9	Fyte et al, 1990
	Medium pore	ZSM-48	10	5.3-5.6	Schelenker et al, 1978
		ZSM-5	10	5.3-5.6	Van Koningsveld et al, 1990
				5.1-5.5	
	Small pore	CaA	8	4.2	Meier and Olson, 1987
		SAPO-34	8	4.3	Lok et al, 1987

They visualized the formation of crystalline and microporous solids possibly due to some structure directing agents which has an exceptional catalytic and gas sorption properties and shows superior properties on different post synthesis treatment. Later on it was proved by scientists all over the world, with term “Metal Organic Frameworks or MOF” which was coined by O.M. Yaghi et al. in 1995. Later on in the same year Kitagawa et al. reported 3D MOF in 1995 and in 1999, HKUST-1 and MOF-5 was synthesized and thereafter the research has grown beyond rapidly.

### **2.2.1. BRIEF HISTORY OF THEIR SYNTHESIS**

Numerous reports have been presented on various literature surveys to find the catalytic activity, catalysts textural properties, and pyrolysis product distribution [4]. Different reports have been presented by a several authors which give challenging outputs about catalytic pyrolysis of polypropylene on catalysts such as ZSM-12, PZSM-5 , HMOR , HUSY, DeLaZSM-5 , BEA, FCC, MOR, ZSM-5, HZSM-5, US-Y, Beta, pillared clay and two mesoporous catalysts MCM-41 and SAHA. Metal Organic Frameworks (MOFs) are a new class of an ordered porous hybrid materials that exhibit exquisite properties [4]. This class of permeable materials, structured by blend of natural linkers with metal centres, offers flexibility in synthesis methods and design and with exceptional inward pore volume, high surface region and pore size crossing the limits of any possible known permeable adsorbents (activated carbon, zeolites, mesoporous silica).

### **2.3. VARIOUS SYNTHESIS PROCESS OF THESE ADSORBENTS**

The various synthesis process of Al-MCM-41 adsorbents are as follows :-

#### **2.3.1. SYNTHESIS OF Al-MCM-41**

Numerous routes and methods have been reported for synthesizing of Al-MCM-41 which vary just in the utilization of templates, time, temperature of reaction and mixture's pH and aluminum source. Few literatures allude to the impact of MCM-41 on polystyrene. Thus we have endeavored to prepare Al-MCM-41 catalyst by hydrothermal route; characterizing them and reporting the different activities of the catalysts on polystyrene and make comparison of the results obtained.

**Table 2.2.** Chemical composition of Al-MCM-41 (present work and literature) [4]

Sample	Si/Al ratio	Al Source	Si Source	Template
Al-MCM-41 (sol-gel)	35.6	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	N-Cetyl-N,N,N-trimethylammonium bromide ( $C_{19}H_{42}BrN$ )
Al-MCM-41 (sol-gel)	40	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium chloride ( $C_{16}H_{33}(CH_3)_3NCl$ )
Al-MCM-41 (sol-gel)	26	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	n-Tetradecyltrimethylammonium bromide
Al-MCM-41 (sol-gel)	35.6	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium bromide
Al-MCM-41 (sol-gel)	26.8	Aluminum Suplhate ( $Al_2(SO_3)_4 \cdot 18H_2O$ )	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium bromide
Al-MCM-41 (sol-gel)	31.9	Sodium Aluminate	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium bromide
Al-MCM-41 (sol-gel)	31	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium chloride ( $C_{16}H_{33}(CH_3)_3NCl$ )
Al-MTS (2)	30	Aluminum isopropoxide (AIP)	Tetraethoxysilane (TEOS)	Hexadecyltrimethylammonium chloride ( $C_{16}H_{33}(CH_3)_3NCl$ )
AL-MCM-41 (hydrothermal)	17.6	Sodium Aluminate	Silica Ludox and tetramethylammonium silicate (TMA Si)	Hexadecyltrimethylammonium chloride / tetramethylammonium hydroxide (TMAOH)
Al-MCM-41 (hydrothermal)	32	Alumina	Silica Cab-O-Sil and TMA Si	Hexadecyltrimethylammonium chloride / ammonia
Al-MCM-41 (hydrothermal)	31.9	Aluminum Suplhate ( $Al_2(SO_3)_4 \cdot 16H_2O$ )	Tetraethoxysilane (TEOS)	N-Cetyl-N,N,N-trimethylammonium bromide ( $C_{19}H_{42}BrN$ )
Al-MCM-41 (hydrothermal)	30	$AlCl_3 \cdot 6H_2O$	Tetraethoxysilane (TEOS)	N-Cetyl-N,N,N-trimethylammonium bromide ( $C_{19}H_{42}BrN$ )

### 2.3.2. SYNTHESIS OF MOFS

Conventionally the MOF was synthesized using solvothermal technique which had no side reaction. The reaction takes place high temperature and in autogenous pressure conditions inside a closed vessel which is normally kept above the boiling point of the liquid.

Thereafter non-solvothermal techniques came into existence, where the reaction takes place in ambient conditions.

Further development has led to new routes of synthesis like, in-situ, high throughput methods and ex-situ crystallization of MOF. With theory of crystallization focus shifted towards low transferring energy and temperature required for crystal synthesis rather than supplying heat source. Such synthesis methods produced compounds with different particle sizes and also different size distribution along with morphologies influencing their properties. There was also need to establish facile, inexpensive, rapid and commercially viable synthesis routes.

## **2.4. AN OVERVIEW OF CHARACTERIZATION TECHNIQUES**

The various characterization techniques used are SEM, PXRD, BET surface area analysis, Particle size distribution, thermogravimetric analysis.

### **2.4.1. SCANNING ELECTRON MICROSCOPY (SEM)**

Scanning Electron Microscopy (SEM), is an electron microscopy technique that provides detailed information about a sample's surface morphology, composition and electrical conductivity. A high energy electron beam is directly fired towards the sample surface, from electron gun, fitted with a tungsten filament, cathode which interacts with the atoms which make up sample, produce back scattered electrons, secondary electrons, characteristic light, X-rays, specimen current & transmitted electrons which can be detected with the help of some special sensors to give a high resolution images of the sample surface morphology. Tungsten is so used because of high melting point and low cost.

**Sample Preparation:** All the samples for SEM analysis, prior to investigation, were dried for 10 hours in order to remove traces amount of treatment solvent and moisture which can produce inferior quality images. Specific slot in the specimen chamber was covered with a carbon tape, on to which the powder was simply attached. The specimens were coated with

platinum, in order to increase conductivity of sample and to obtain superior quality image, by low vacuum sputter coating[14]. The coated samples of membrane was placed over specimen slot and locked into the chamber for further analysis. SEM used in this present work was SEM, JEOL JSM-6480 LV facility.

#### 2.4.2. X-RAY DIFFRACTION

X-ray diffraction is a powerful characterization tool which provides information regarding the crystal structure, physical properties of thin films and crystalline materials where, the scattered intensity of X-ray beam which is generated upon hitting the sample, is measured as function of the incident angle, scattered angle, wavelength and polarization. Though scattering of beams from sample leads to the destructive interference, there are some specific directions in which they sum up to give diffraction pattern which is governed by Bragg's Law given by

$$2.d \sin\theta = n.\lambda \quad (2.1)$$

where  $\theta$  is incident angle,  $d$  being spacing between the planes,  $n$  being any integer and  $\lambda$  being the wavelength of the incident beam.

**Sample Preparation:** Prior to investigation, all the sample for XRD analysis were dried for 10 hours, to remove traces amount of treatment solvent, moisture which can generate distorted patterns. The powder was carefully placed in the sample slot to make a powder bed and the surface of powder was smoothened. Then they were subjected to X-ray diffraction in different  $2\theta$  angles ranging from  $5^\circ$  to  $75^\circ$  with a ramp of 0.05 degrees and a rate of scanning  $1^\circ/\text{minute}$  [14].

X-ray diffraction machine used in this present work was XRD, Philips Analytical, PW-3040 equipped with graphite monochromatized  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ).

### 2.4.3. BET SURFACE AREA ANALYSIS

Brunauer, Emmett and Teller (BET), in 1938, introduced a new concept in the field of surface science that describes the multi-layer adsorption of gases above the surfaces. This theory was later used to estimate the total surface area of different material and is given by equation

$$\frac{x}{V(1-x)} = \frac{1}{cv} + \frac{x(c-1)}{cv} \quad (2.2)$$

where  $x$  being relative pressure  $P/P_0$ ,  $V$  being the STP volume of the adsorbate,  $v$  is the STP volume of the amount of adsorbate required to form monolayer,  $c$  being the equilibrium constant.

**Sample preparation:** the samples for the surface area analysis were dried at 100°C for 3 hours before outgassing. The sample in powder form was directly used. Then the sample was degassed at 150°C for about 90 minutes.

The BET surface area analyzer utilized in this project was Quantachrome - Autosorb-1.

### 2.4.4. THERMAL GRAVIMETRIC ANALYSIS

Thermogravimetric Analysis (TGA) or Thermal Gravimetric Analysis is an important laboratory technique employed to predict the thermal stability of any material by measurement of the change of its weight with respect to the increase in temperature with a controlled atmosphere. Based on the data obtained like temperature, weight loss and rate of temperature change, proportion of organic and inorganic materials in sample, the information on absorbed moisture and solvent residue apart from the degradation temperature can be obtained after performing the required transformation of the obtained results. Normally TGA is conducted either in inert environment using nitrogen gas or atmospheric environment in a pre-programmed gas flow rate. Thermogravimetric analyzer used in this present work was from Shimadzu (DTG 60 H).

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## 3. EXPERIMENTAL WORKS

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### 3.1. INTRODUCTION

This chapter describes the various experimental protocols followed, materials and resources utilized and a short description of logic behind the idea of pursuing the said experiments wherever found essential. The chapter is segregated into four main sections for ease in explaining: sequentially and logically.

### 3.2. CHEMICALS UTILIZED

All the different chemicals used in this work were obtained from various commercial sources and were utilized without any further purification unless and until specified. All the chemicals along with their molecular formula and manufacturer name are listed below

Major chemicals are [14] ; 1,4-benzene dicarboxylic acid (commonly known as terephthalic acid) [ $C_8H_6O_4$ , Loba Chemie Private Limited, India], Copper (II) Nitrate trihydrate [ $Cu(NO_3)_2 \cdot 3H_2O$ , Merck Specialities Private Limited, India], Chromium (III) nitrate nonahydrate [ $Cr(NO_3)_3 \cdot 9H_2O$ , Loba Chemie Private Limited, India], Hydrofluoric acid [HF, Merck Specialities Private Limited, India], N, N-dimethylformamide [ $C_3H_7NO$ , Merck Specialities Private Limited, India], n-hexane [ $C_6H_{14}$ , 1, 3, 5-benzenetricarboxylic acid (commonly known as trimesic acid) [ $C_6H_3(COOH)_3$ , Zinc (II) Nitrate hexahydrate [ $Zn(NO_3)_2 \cdot 6H_2O$ , Merck Specialities Private Limited, India], Merck Schuchardt OHG, Merck Specialities Private Limited, India], Ethanol [ $C_2H_5OH$ , Merck Specialities Private Limited, India] and Methanol [ $CH_3OH$ , Merck Specialities Private Limited, India]

The non-isothermal decomposition without and with catalyst was carried out on polystyrene, Trade name: Koylene ADL, Grade AS030N) supplied by Indian Petrochemicals Corporation Limited, Vadodara, N-cetyl-N,N,N-trimethylammonium bromide ( $C_{19}H_{42}BrN$ ) (98%, Loba Chemie, India), tetraethoxysilane (TEOS (98%), Merck, Germany),

Tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, aluminium isopropoxide (AIP (>98%), Acros Organics, India), , propan-2-ol (PrOH) ((99.5%), Merck, India), 25% ammonia solution ((99.5%), Merck, India), NaOH, Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ , Merck, India) were also used in the synthesis process [4].

### **3.3. EXPERIMENTAL WORKS**

The various experimental works conducted in the present work are as follows :-

#### **3.3.1. CONVENTIONAL Al-MCM-41 ADSORBENTS**

The conventional Al-MCM-41 adsorbents are prepared by two methods.

##### **3.3.1.1. SYNTHESIS OF Al-MCM-41 BY SOL-GEL PROCESS**

The Sol-gel Al-MCM-41 was synthesized according to the given procedure [4]. In the present work, N-cetyl-N,N,N-trimethylammonium bromide ( $\text{C}_{19}\text{H}_{42}\text{BrN}$ ) was utilized as the template which supplanted hexadecyltrimethylammonium bromide or tetradecyltrimethylammonium bromide. The procedure is as follows :

1. The catalyst was synthesized by using  $\text{C}_{19}\text{H}_{42}\text{BrN}$ ; aluminium isopropoxide, tetraethoxysilane, propan-2-ol (PrOH), 25% ammonia solution and deionized water. 3.7% solution of AIP was prepared in PrOH and was mixed in a glass tube in an ultrasonic bath for 10–15 minutes.
2. The  $\text{C}_{19}\text{H}_{42}\text{BrN}$  template (1.29 gm) was mixed along with 69.2 gm of water and the mixture was warmed up until it is completely dissolved.
3. Then it was cooled down before adding to it 5 mL of ammonia.
4. A mixture of suitable volume of AIP solution and TEOS (5 mL) was added dropwise to the above mixture, while stirring, for a 15 minutes to get actual molar ratio. The molar composition of the gel that was finally obtained was 1TEOS:1/xAIP: 0.147  $\text{C}_{19}\text{H}_{42}\text{BrN}$ : 3.04 $\text{NH}_3$ :160 $\text{H}_2\text{O}$ : yPrOH, where  $x = 30$  and  $y = 2.89$ .
5. Then the suspension was kept for 1–1.2 h under continuous stirring.



6. Then, by filtration, the products were recovered and then washed thoroughly with 2 L of deionized water.
7. Then after drying at 343 K, the sample was calcined at 823 K in air for 12 h, maintaining a heating rate of 2 K min<sup>-1</sup> during the period of time.

### **3.3.1.2. SYNTHESIS OF Al-MCM-41 BY HYDROTHERMAL METHOD**

The hydrothermal Al-MCM-41 [4] synthesis was prepared accordingly

1. C<sub>19</sub>H<sub>42</sub>BrN (0.6 g) and NaOH (0.40 g) were first dissolved in about 32 mL deionized water and 3.85 gm of TEOS was then added to this mixture.
2. Aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 16H<sub>2</sub>O) (0.37 g) was dissolved separately in about 10mL of deionized water in a separate beaker.
3. Then this was added to the reaction mixture and continuous stirring was done for 105 min at ambient temperature.
4. The obtained mixture was then stirred and was heated at 80°C for next 20 minutes.
5. Then the mixture was stirred overnight which was then transferred to Teflon-lined autoclave and was kept at 150°C for about 12 hours. The molar composition of the gel thus obtained was 1.0SiO<sub>2</sub>:0.031Al<sub>2</sub>O<sub>3</sub>:0.27Na<sub>2</sub>O:0.089CTA<sup>+</sup>:130H<sub>2</sub>O.
6. The synthesized products were then recovered by filtration and were washed thoroughly with 2 L of deionized water.
7. The samples, after drying at 343 K, were then calcined in air at 823 K for about 12 hours by maintaining heating rate of 2 K min<sup>-1</sup> during the period of time.

### **3.3.1.3. CHARACTERIZATION**

1. Al-MCM-41 catalysts, that was obtained by hydrothermal process, were characterized by the X-ray diffraction (XRD) analysis for 2θ angles ranging from 5° to 85° with a ramp of 0.05 and step time of 0.5 s.

2. The surface area pore size distribution were measured using the BET surface area analyzer using Nitrogen adsorption isotherm at temperature of 77 K. The relative pressure was in the range 0.1 - 1. The value of the C (the constant of BET equation) was taken as 71.28 for hydrothermal process.
3. Then the samples were outgassed thoroughly for 3 hours at a temperature of 300 °C to remove the volatile materials and moisture adhering to it.
4. Then the particle size analysis was done using the laser particle size analyzer

### **3.3.2. MOF ADSORBENTS**

The MOF adsorbents are prepared according to the following procedure :-

#### **3.3.2.1. SYNTHESIS OF CU-BTC OR HKUST-1**

1. A solution of 1.0 g of organic linker 1, 3, 5-benzenetricarboxylic acid was dissolved with 30 ml of a 1:1 mixture of ethanol/N, N-dimethyl formamide (DMF).
2. 2.077 g of solution of copper (II) nitrate trihydrate was then dissolved separately in 15 ml water.
3. Both solutions were mixed and was stirred continuously for 10 minutes and then transferred into teflon-lined stainless steel autoclave which was heated for 10 hours at 373K.
4. After the completion of reactions, the autoclave was allowed to cool down to room temperature naturally.
5. The blue colored obtained were isolated by filtration using the standard Whatman filter paper.
6. The products collected from various batches were then mixed and was then treated with methanol inside a soxhlet apparatus to remove all solvated DMF and the traces of impurities.

7. Finally the product was dried at 100°C for 30 minutes and was then stored inside the desiccator.
8. During post synthesis treatments, the Cu-BTC was subjected to methanol separately to study the stability characteristics. The crystals were treated for 3 hours with methanol at 60°C and for 3 hours under continuous stirring condition.

### **3.3.3. AL-MCM-41 ADSORBENT (WITH CHANGED SI SOURCE)**

The TEOS (Si- source) used for the synthesis of the Al-MCM-41 adsorbents is very expensive although it produces good results. But instead, in this present work we have focused on the use of a much cheaper source of silicon to prepare Al-MCM-41 catalyst. Instead of tetraethoxysilane, 2.63 g of Sodium meta silicate was used as the source of silica and the same procedure was followed as in case of conventional Al-MCM-41 synthesis. The product obtained was washed thoroughly with 2 L of water and was dried at 373 K. The final product was obtained after it was calcined for 10 hours at 873 K with heating rate of 2 K min<sup>-1</sup>. Then the characterization of the product was done by different techniques.

### **3.4. APPLICATION: POLYSTYRENE DEGRADATION BY CU-BTC CATALYST**

The decomposition reactions [4] both, thermal as well as catalytic, were carried out in the TGA instrument in nitrogen atmosphere with temperature range of 298-873K. The flow rate of nitrogen was maintained at 35–50 mL/min. The sample provided was crushed into very fine pieces of -40/+60 mesh size and was directly fed to the TGA instrument. A sample holder made up of Platinum crucible (150 mL) was used. The decomposition reaction was done for different wt% of the catalysts (between 0–33 wt%) at 10 Kmin<sup>-1</sup>. Catalytic decomposition experiments were carried out further using 18.5 wt% at different heating ramp of 5 Kmin<sup>-1</sup>.

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## 4. RESULTS AND DISCUSSIONS

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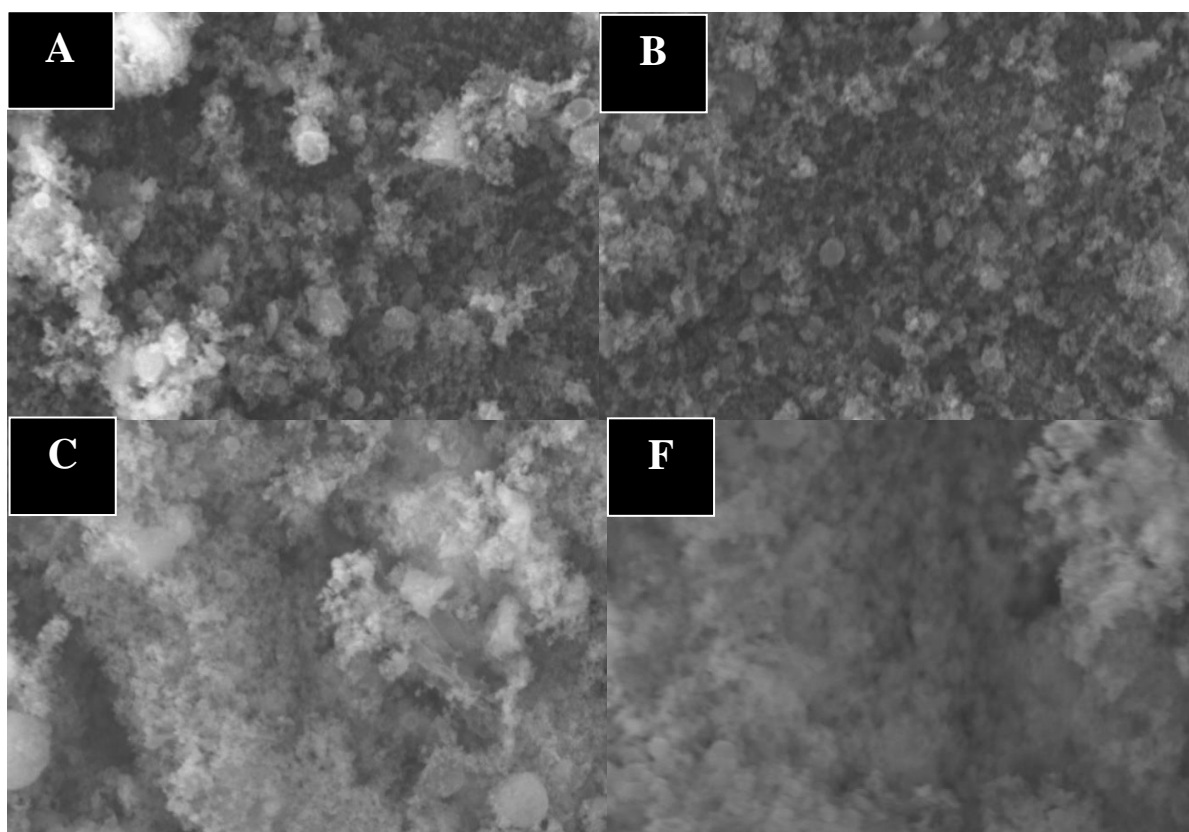
The different results obtained are studied and compared with literature.

### 4.1. AL-MCM-41 ADSORBENTS

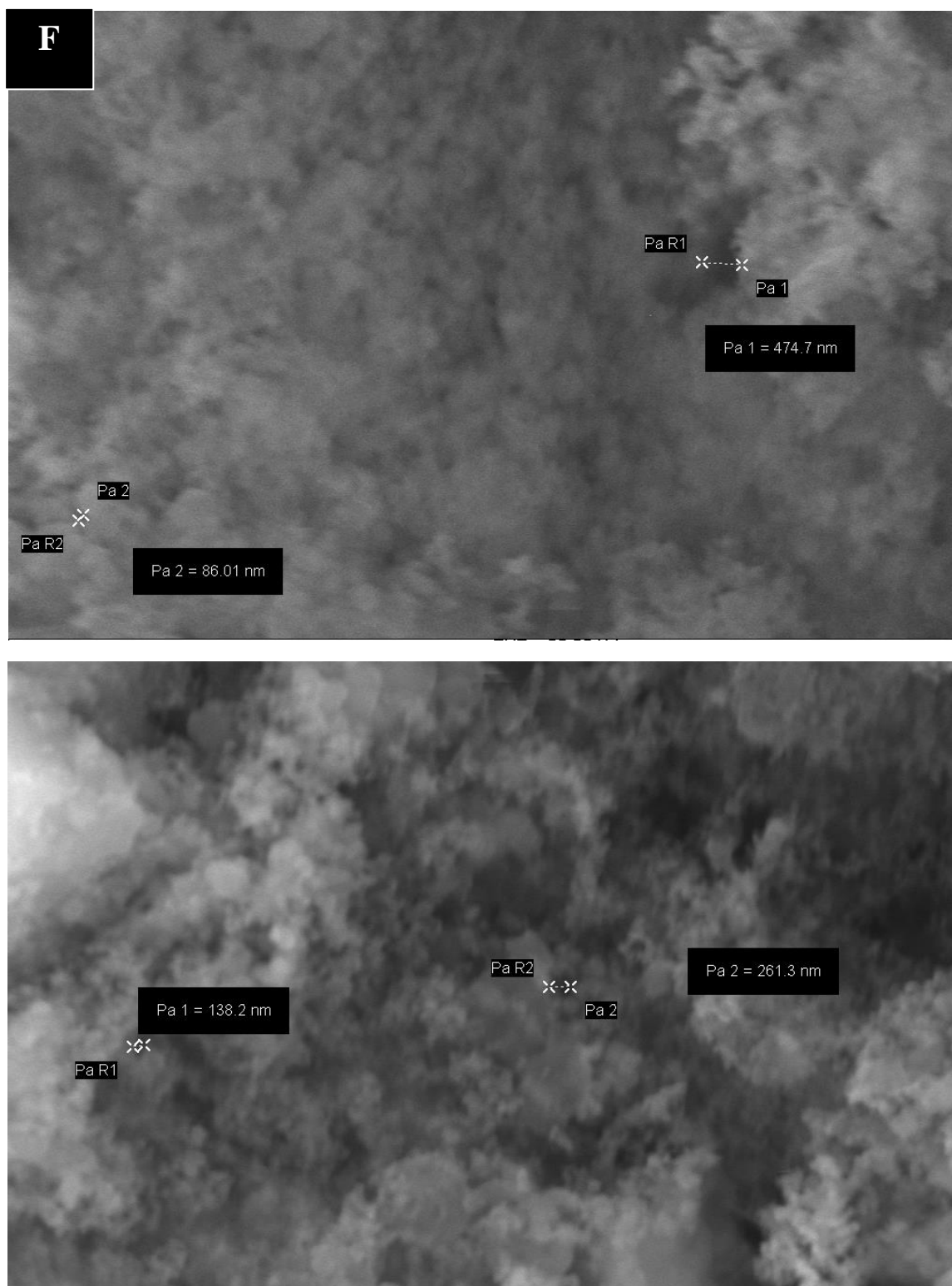
The characterization of Al-MCM-41 was done and the results obtained were as follows:-

#### 4.1.1. SURFACE MORPHOLOGY OF Al-MCM-41 SAMPLES

SEM images of the synthesized Al-MCM-41 samples are shown in Figure 4.1. It shows that the sample resembles the class of zeolites but they don't have uniformity in size. Thus it categorizes Al-MCM-41 as an amorphous powder material rather than a crystalline structure with uneven pore size distributions, large pore volumes or void volumes and large surface area.



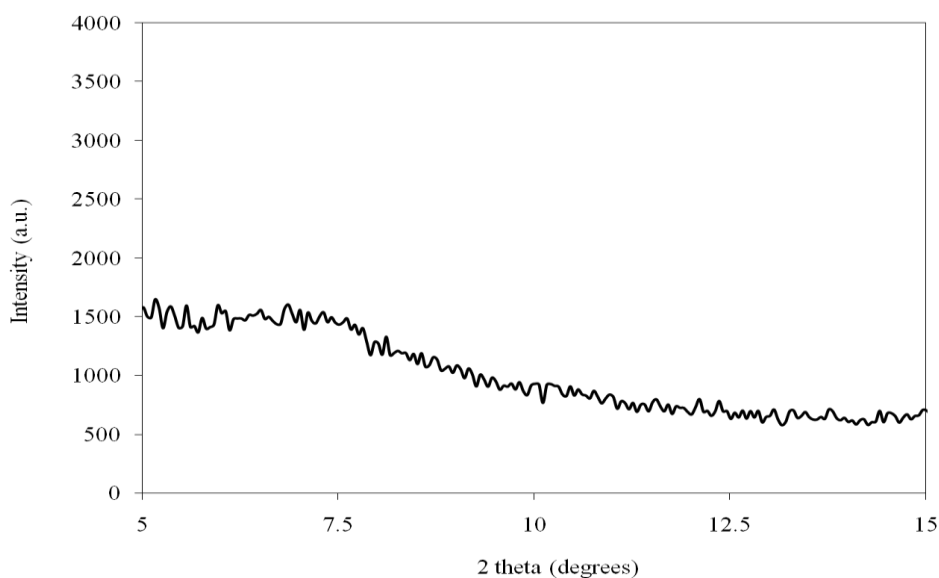
**Figure 4.1:** SEM Images of as-synthesized MCM-41 (Al) sample (A, B) at 2  $\mu\text{m}$  resolution and 4000 X magnification (C, D) at 1  $\mu\text{m}$  resolution and 10000 X magnification



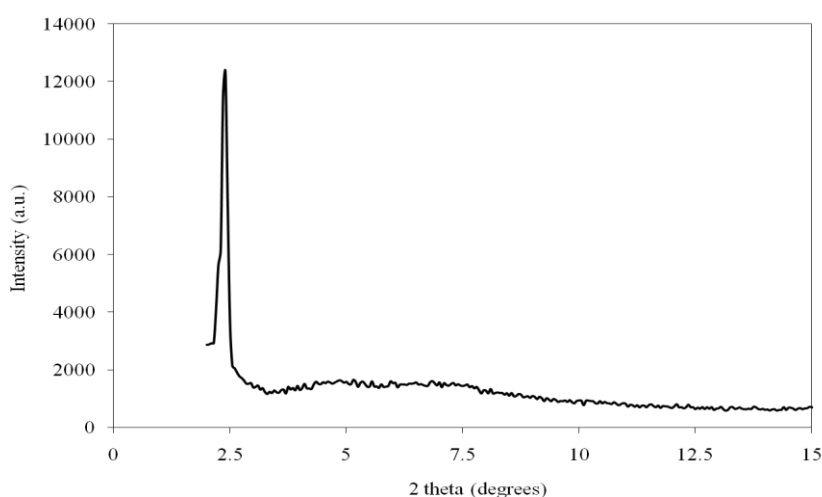
**Figure 4.2** : SEM Images of as-synthesized MCM-41 (Al) sample (**E, F**) at 1 $\mu$ m resolution and 10000 X magnification. (labelling of the images to know the approximate relative size distribution)

#### 4.1.2. PXRD PATTERNS OF AL-MCM-41 SAMPLES

The PXRD patterns (Figure 4.3) of the sample show a very low angle with an sharp diffraction peak which is in  $2\theta = 2.1 - 2.408$  region (figure 4.4 ). No higher angle were found to be observed which indicates that the aluminium containing crystalline phase is absent within the catalyst.



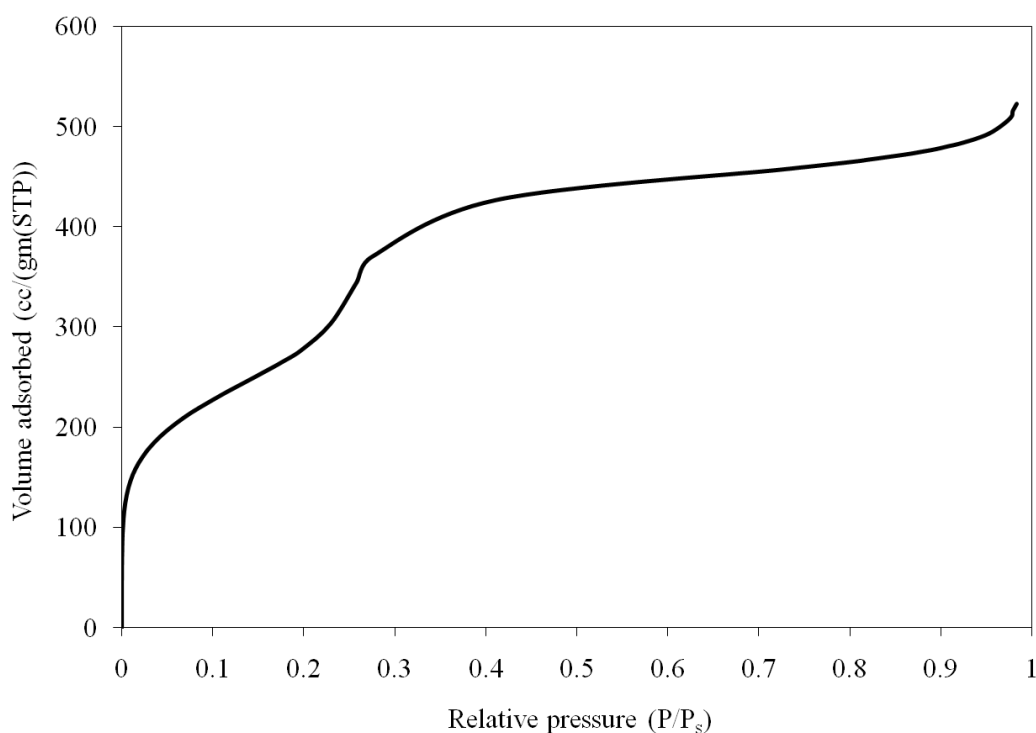
**Figure 4.3 :** Powder X-ray diffraction analysis of as-synthesized Al-MCM-41 sample



**Figure 4.4 :** Powder X-ray diffraction analysis of as-synthesized MCM-41 (Al) sample [4]

#### 4.1.3. BET SURFACE AREA ANALYSIS OF AL-MCM-41 SAMPLES

The catalysts show similar behavior as that of the type IV isotherm classified according to the IUPAC classification. This shows that it is a typical mesoporous material. The isotherm, though completely reversible, it is not prominent with the catalyst produced by hydrothermal route; the sol-gel method rather shows hysteresis at a very high relative pressure ( $P_s/P_o$ ) as pore filling occurs, which indicates uniformity in size of unidirectional tubular mesopores.



**Figure 4.5 :** BET isotherm of Al-MCM-41 sample

BET surface area = 1200 m<sup>2</sup>/gm

Langmuir surface area = 950 m<sup>2</sup>/gm

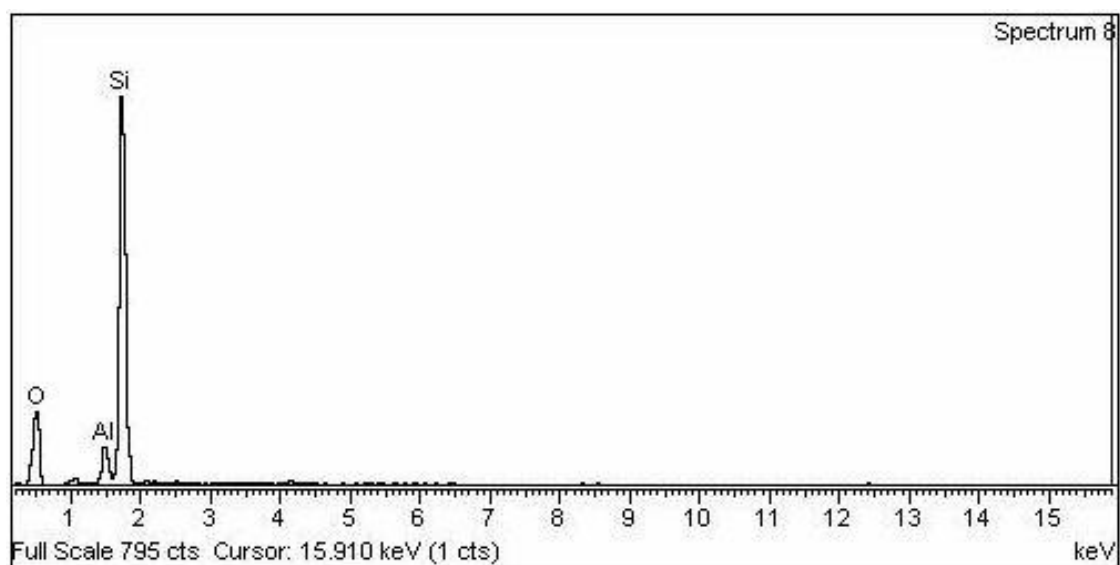
Pore size distribution = 5 to 35 nm

#### 4.1.4. PARTICLE SIZE ANALYSIS OF AL-MCM-41 SAMPLES

The Energy dispersive X-ray technique was used and it was found that the samples have higher Si/Al ratio indicating that the sample produced is a silica based catalyst.

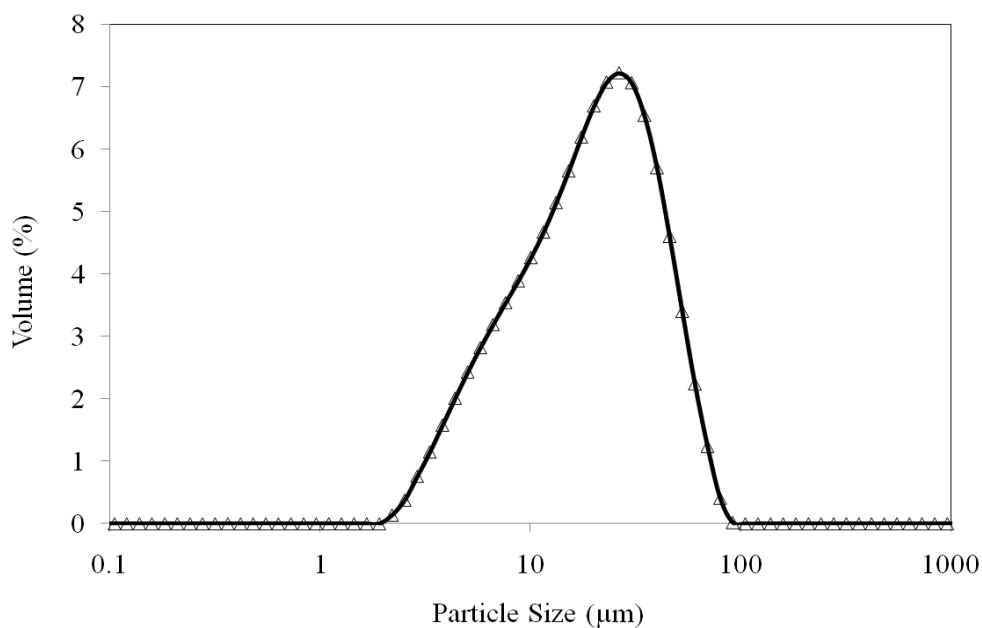
**Table 4.1** : Elemental analysis of the sample represented in wt %

Element	Weight %	Atomic %
O K	43.37	57.28
AL K	3.95	3.09
Si K	52.68	39.63
Totals	100.00	100.00



**Figure 4.7** : Energy dispersive X-ray image of the synthesized sample





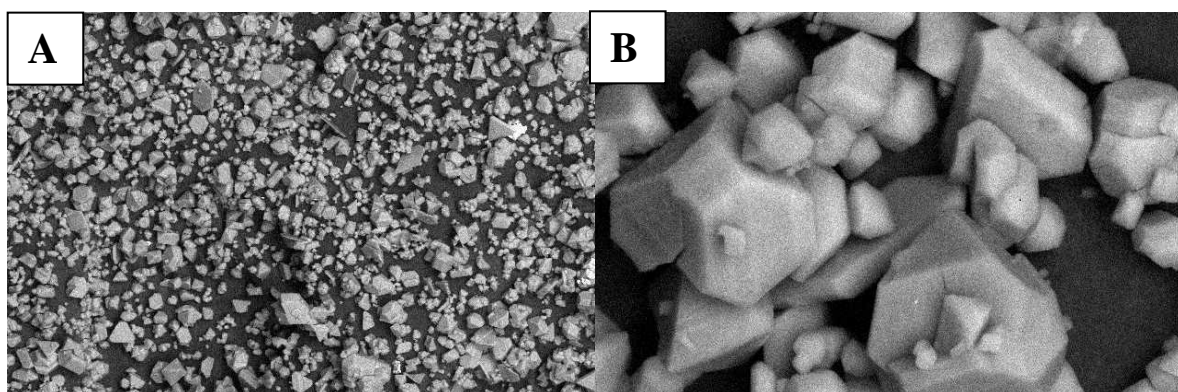
**Figure 4.8 :** Particle size analysis of Al-MCM-41 samples

## 4.2. CU-BTC ADSORBENTS

The characterization results of the Cu-BTC adsorbents are as follows :-

### 4.2.1. SURFACE MORPHOLOGY OF CU-BTC SAMPLES

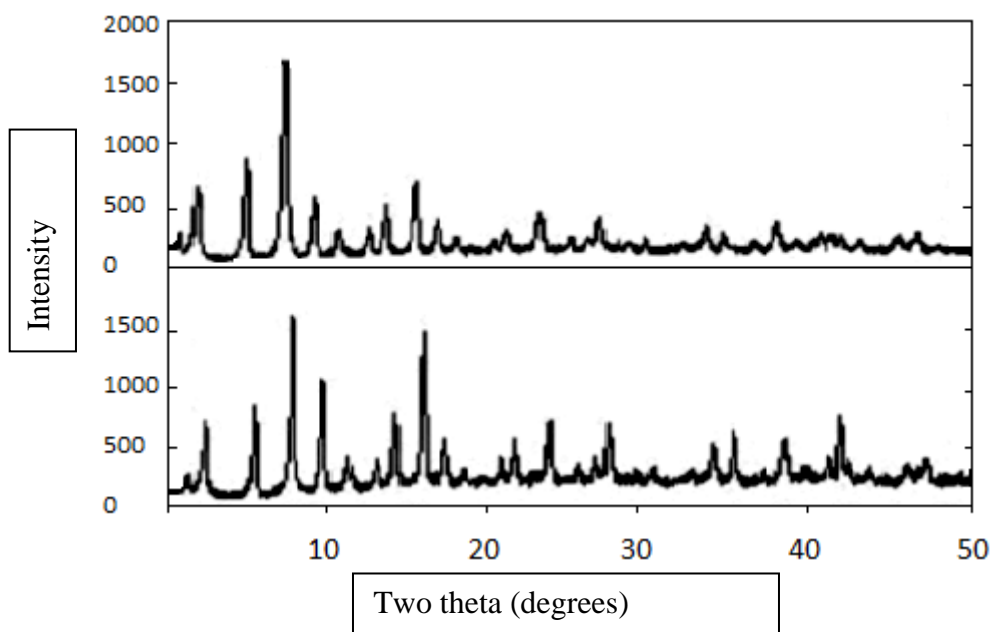
SEM images of the synthesized Cu-BTC are shown in Figure 4.9. It is evident that Cu-BTC is octahedral in nature along with different crystal sizes.



**Figure 4.9 :** SEM images of As Synthesized Cu-BTC at 20 μm resolution A) 100 μm resolution and 200X magnification B) 2000X magnification and 10 μm resolution

#### 4.2.2. PXRD PATTERNS OF CU-BTC SAMPLES

Powder XRD patterns are the fingerprints of any type of solid crystalline material on earth. They also give us an idea of the chemical composition and the level of the pattern interference due to the impurities which can be used as a measurement of determining the effect of treating with solvents.



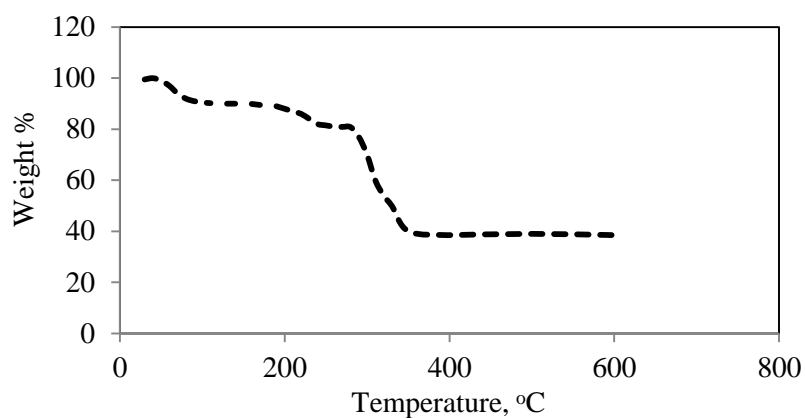
**Figure 4.10 :** The PXRD patterns of various samples

The peaks which are formed at 11°, 13°, 14° and 17° are the characteristic peaks of Cu-BTC confirming the formation of Cu-BTC phase. Methanol treated sample shows better refinement in XRD peaks as the original sample and the level of amorphous character in profile decreases with the subsequent treatment with hot methanol.

#### 4.2.3. THERMOGRAVIMETRIC ANALYSIS OF CU-BTC SAMPLES

The TGA provides us with the information about the thermal stability of the synthesized sample. Figure 4.11 depicts the TGA profile of the sample of Cu-BTC synthesized. The TGA profile shows 3 distinct weight loss steps for the given samples. In the temperature range of 25-125°C, the weight loss is mainly due to the removal of moisture and due to the trapped methanol. In the 2nd step from 125°C to 280°C (a horizontal plateau) the weight remains

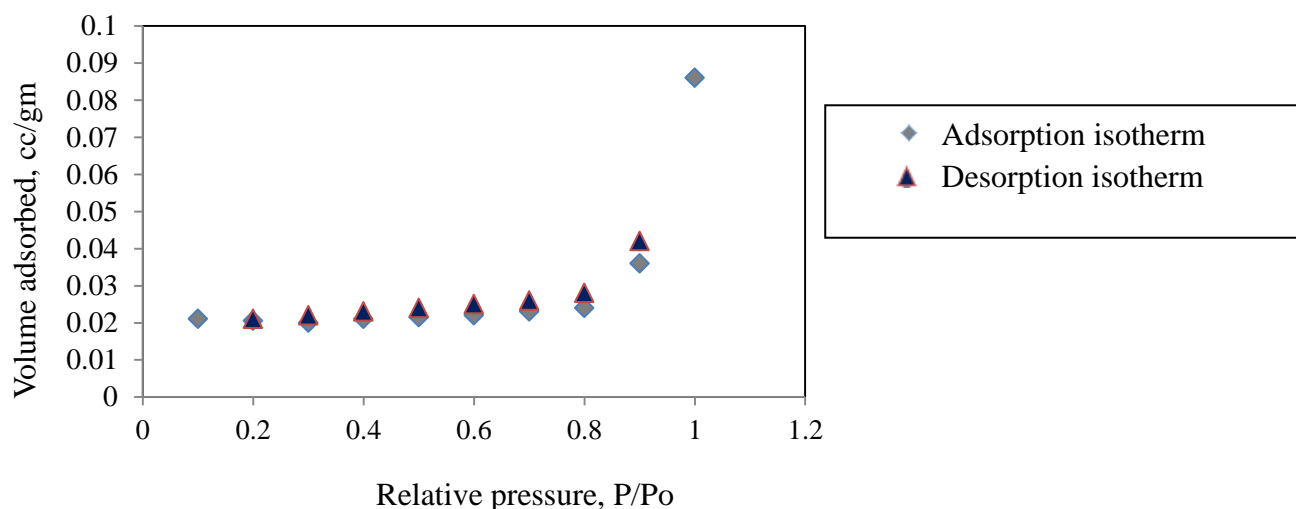
almost constant. Beyond 280°C, all samples, irrespective of the post-synthesis treatments, they start degrading permanently. Thus, the temperature mustn't go beyond this maximum value



**Figure 4.11** : TGA patterns of various samples of Cu-BTC

#### 4.2.4. BET SURFACE AREA ANALYSIS OF CU-BTC SAMPLES

BET isotherm was studied in the relative pressure range of 0.1 - 1. From the figure showing complete adsorption and desorption curves, it can be interpreted that no hysteresis was observed and hence we can safely assume pores of the Cu-BTC are cylindrical in shape. The surface area was found to be around 1500 m<sup>2</sup>/ gm.



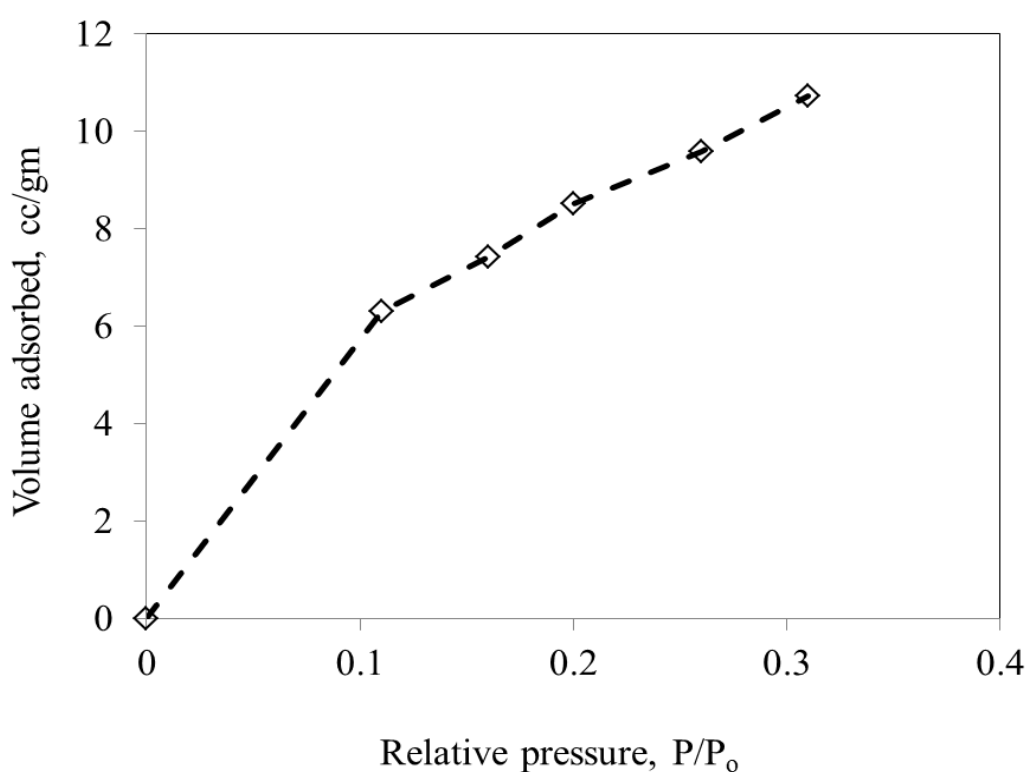
**Figure 4.12** : The BET isotherm that is obtained for the 'methanol treated Cu-BTC' sample

### 4.3. AL-MCM-41 (ADSORBENTS WITH CHANGED SI- SOURCE)

The characterization results of Al-MCM-41 (with changed Si source) are as follows :-

#### 4.3.1. BET SURFACE AREA ANALYSIS OF AL-MCM-41 SAMPLES

BET surface area analysis was done at 77 K in nitrogen atmosphere. The isotherm is shown in Figure 4.13. The catalysts behavior is similar as that of the type IV isotherm classified according to the IUPAC classification which shows that it is a typical quality mesoporous material.



**Figure 4.13 :** BET isotherm obtained for AL-MCM-41 with different Si-source

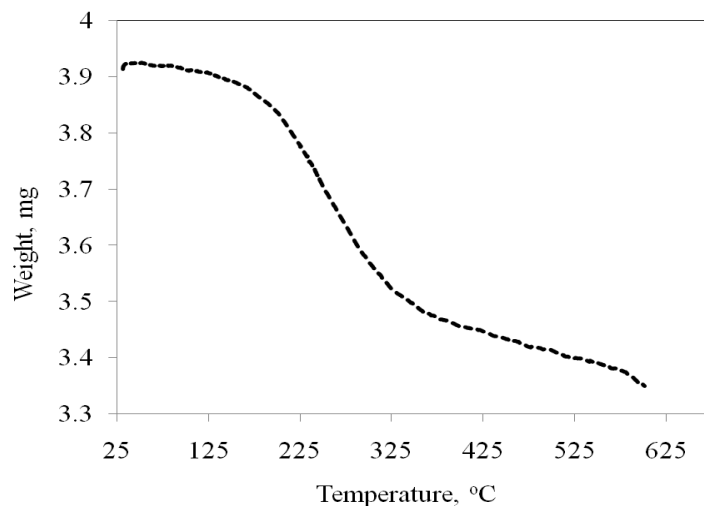
Area = 3.681E+01 m<sup>2</sup>/g

Slope = 8.854E+01

C = 1.558E+01

#### 4.3.2. THERMO GRAVIMETRIC ANALYSIS OF AL-MCM-41 SAMPLES

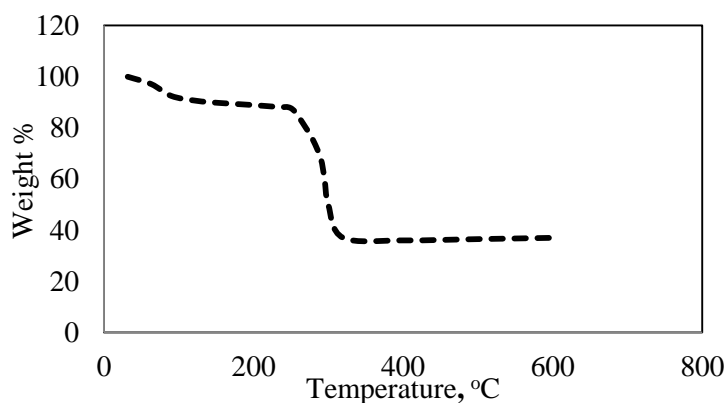
The TGA provides us with the information about the thermal stability of the sample. Figure 4.14 depicts the TGA profile of the sample of Cu-BTC synthesized.



**Figure 4.14** : TGA analysis obtained for Al-MCM-41 with different Si-source

#### 4.4. POLYSTYRENE DEGRADATION USING CU-BTC CATALYST

The experiments were conducted for catalytic as well as non-catalytic degradation of polystyrene in TGA. The maximum degradation temperature is reduced on application of catalyst as shown through the DTG curves (Figure 4.15). The maximum shifting of  $T_m$  are observed to be 68 K and 114 K for catalysts. It was observed that polystyrene in presence of Cu-BTC catalyst disintegrated at temperature below 300 °C.



**Figure 4.15** : TGA pattern of decomposition of polystyrene with Cu-BTC catalyst

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## 5. CONCLUSIONS AND FUTURE RECOMMENDATIONS

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In this project work, two relatively new porous materials *viz.* MCM-41 and Cu-BTC were synthesized, following standard recipes. Detailed characterizations were successfully carried out to ascertain the products formed, following techniques like Scanning Electron Microscopy (SEM), Powder X-ray diffraction (PXRD) analysis, BET surface area analysis and Laser particle Size Analysis. SEM images revealed contrasting surface morphology for the synthesized products. MCM-41 showed discontinuity in crystal formation with imperfections and distribution in porous networks whereas Cu-BTC showed a much uniform growth of crystals with regular sizes, shapes and porous network. Powder X-ray diffraction also corroborated the findings and it showed that as-synthesized MCM-41 was amorphous in nature whereas Cu-BTC was crystalline. The BET surface area measurements data showed that the specific surface area of MCM-41 was *ca.* 1200 m<sup>2</sup>/gm and for Cu-BTC, the value stood at *ca.* 1500 m<sup>2</sup>/gm. Laser particle size analysis for MCM-41 also showed a wider distribution of particles, using water as the dispersant medium. A new variant of MCM-41 was also synthesized by replacing the costly Si source (Tetraethyl orthosilicate) with cheaper source (Sodium silicate solution). Surface area data showed a much lesser surface area of *ca.* 36 m<sup>2</sup>/gm. This variation could be attributed to post synthesis treatments and presence of cetyl tertiary butyl ether (CTAB) in the framework as a template. Owing to higher surface area Cu-BTC was used for studying the degradation of polystyrene. The study showed affirmative results in the degradation temperature of polystyrene.

## **FUTURE WORKS :**

The present work can be extended to carry out further research in the following area:

- (a) Synthesizing newer variants and/or derivatives of zeolites and metal organic frameworks by judiciously altering the metal ions, Si/Al ratio, organic/inorganic linkers and synthesis conditions.
- (b) Microwave assisted synthesis approach for more benign synthesis chemistry for the formation of reaction products (with fewer by-products) and crystal imperfections.
- (c) Improving post-synthesis treatments for higher yield in surface area.
- (d) Detailed polymer degradation study using MCM-41 and Cu-BTC, including product distribution.

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